



TITLE:

The Synthesis and Chemical Behaviours of Dioxaspiroheptane

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CITATION:

Furukawa, Kiyohisa ...[et al]. The Synthesis and Chemical Behaviours of Dioxaspiroheptane. Bulletin of the Institute for Chemical Research, Kyoto University 1953, 31(3): 222-223

ISSUE DATE:

1953-05-30

URL:

<http://hdl.handle.net/2433/75319>

RIGHT:

From equation (6), it is reasonably expected that the acidity of alcohol is one of the most important factors that affect the rate of vinylation.

As is shown in our results, since the lower acidic alcohol is faster vinylated, it can be assumed that the undissociated alcohol does participate in the actual vinylation.

If the sodium atom in an alcoholate, NaOR, is highly ionized, the π -complex cannot be formed, because the sodium is most stable in its ionic form, Na⁺.

Thus phenol deprives the isobutylate of the sodium atom; but the sodium in phenolate is so highly ionized that the reaction (1) cannot occur, vinylation being markedly retarded.

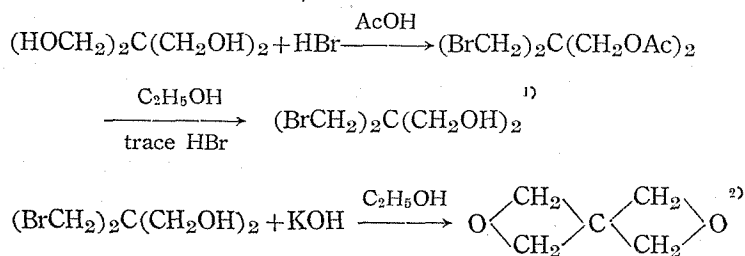
It will be well understood from the similar consideration that the vinylations of the more acidic compounds, *e.g.* acetic acid or phenol can be performed effectively through their undissociated salts such as Hg, Cd, or Zn salt instead of alkali salts.

15. The Synthesis and Chemical Behaviours of Dioxaspiroheptane

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Synthesis of Dioxaspiroheptane (D.A.H.).



1) Beyaert, Hansens: *Natuurw. Tijdschr.* **22**, 249-69 (1940); *C.A.*, **37**, 5373 (1943).

2) Backer, Schurink: *Rec. trav. chim.*, **53**, 812 (1934).

According to the above schema, the authors have synthesized dioxaspiroheptane in 20% yield. D.A.H. (m.p. 89°C) is sublimable in crystal with slight camphor-like odour, easily soluble in water and alcohol, and slightly soluble in ether.

Polymerisation. When 0.5184 g. of D.A.H. was heated at 150°C for 6 hrs. with 0.0725 g. of caustic potash in sealed tube, reddish brown clear resinous product was obtained. This resin is hard and brittle. This resinous product was crushed and washed by hot water. It is insoluble in ordinary solvents and chars slowly at about 300°C without showing melting point.

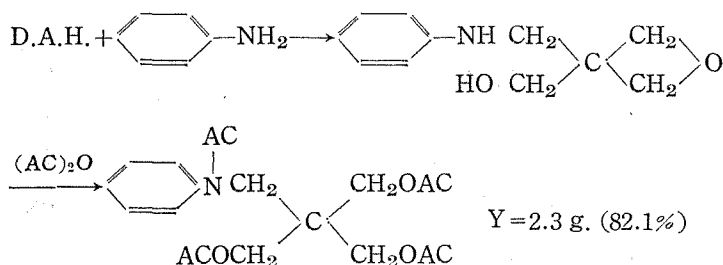
Reaction of D.A.H. with aniline. D.A.H. (0.74 g.) was heated with 4.1 g. aniline at 190~200°C for 12 hrs. and the excess aniline was removed by vacuum distillation. The obtained semi-solid product was acetylated with acetic anhydride and colourless crystal (m.p. 165.5-166°C) was obtained.

Analytical value of the acetylated product:

Calcd. for $C_{19}H_{25}O_7N$ N, 3.69 ; Mol. Wt., 379

Found N, 3.56 ; Mol. wt., 351

From the above data it can be concluded that the reaction has proceeded in the way as follows:



The authors have also attempted the reactions of D.A.H with Grignard reagent, Na-ethylacetoacetate or higher alcohol, but no reaction can be recognized.

It is surprising that the D.A.H.-ring is very stable and unreactive compared with the analogous epoxy-ring compounds.

16. Studies on the Synthesis and Reactions of Ethyl α -Formyl Stearate

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α -Formyl-compound of fatty acid ester is generally produced by the reaction between fatty acid ester and ethyl formate using metallic sodium or sodium alcoholate as catalyst. Many examples of this α -formylation reaction are well known about lower fatty acid esters, but not about the higher.

Therefore the authors have attempted this reaction with ethyl stearate and succeeded in the synthesis of ethyl α -formylstearate and the authors have further tried some reactions of this α -formylstearate with various passive components.

I. Synthesis of ethyl α -formylstearate.

